

Adsorption by Activated Sugar Charcoal

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY IN
THE UNIVERSITY OF MICHIGAN

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ELROY JOHN MILLER

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An Arbor

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The author wishes to express his sincere appreciation of the kindly interest, valuable suggestions, and helpful advice received from Professor F. E. Bartell during the course of this investigation.

E. J. M.



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ADSORPTION BY ACTIVATED SUGAR CHARCOAL

I. INTRODUCTION

That charcoal has the power of removing substances from solution has been known since 1791. In that year Lowitz¹ found that colored solutions could be completely decolorized by simply filtering them through a layer of charcoal. Since that time charcoal has been extensively used in many industries for the clarifying of solutions.

This property of removing dissolved substances from solutions is possessed by other solids such as kaolin, clay, fuller's earth and finely divided platinum. According to Arrhenius² the suggestion that this phenomenon be called adsorption is due to E. du Bois Reymond. The term adsorption is meant to indicate that the adsorbed substance does not enter into the interior of the adsorbent but is only attracted to its surface. The term adsorption thus excludes the processes of solution (solid solution) and chemical interaction involving primary valence forces.

The greater part of the vast amount of work that has been done in connection with the study of the mechanics of adsorption of substances from solution by charcoal has been done with animal or blood charcoal. In view of the fact that the highly complex blood charcoal and the almost equally complex, but less active, wood or vegetable charcoal are not readily purified, it is not surprising that the results obtained with them have varied greatly in the hands of different investigators.

The recent development of methods for the activation of charcoal^{3,4,5} for the adsorption of gases suggested to us the possibility of preparing from sugar an active charcoal which would be free from the objectionable features of animal charcoal, such as high ash, high nitrogen content, and the necessity of treatment with reagents for its purification, and using this charcoal in a study of the nature of adsorption of electrolytes from solution.

II. EXPERIMENTAL PART

Preparation of Activated Sugar Charcoal

Ten-pound lots of cane sugar were repeatedly recrystallized from conductivity water in order to free the sugar, as far as possible, from inorganic matter, such as calcium, etc. After recrystallization the sugar was carbonized and activated by the following method.

¹ Cf. Ostwald, *Lehrbuch allgem. Chemie*, 2nd Ed. I, 1093 (1891).

² Arrhenius, *Theories of Solutions*, 59, (1913).

³ Lamb, Wilson and Chaney, *J. Ind. Eng. Chem.*, 11, 420 (1919).

⁴ Sheldon, *Phys. Rev.*, 16, 165 (1920).

⁵ Winter and Baker, *J. Chem. Soc.*, 117, 319 (1920).

The sugar was charred in a large platinum dish and ignited at a low red heat to drive off the greater part of the volatile matter. This charcoal was then reduced to granules about the size of a kernel of wheat and heated at a temperature of about 1000° . Under proper conditions a marked increase in activity was obtained. The heating was carried out in 18 mm. silica tubes 30 cm. long, closed at one end. An asbestos box was made to fit over the top of a large Meker burner. Holes were provided in the sides of the box to carry the silica tubes in a nearly horizontal position while a small hole in the top of the box permitted the escape of the burner gases. When the silica tubes were half filled with the charcoal and the filled parts of the tubes heated for a period of 24 to 48 hours, or longer, it was found that the layer of charcoal nearest the open end of the tubes had changed its appearance from a bright, gray black to a dull, dead black and was capable of decolorizing considerable amounts of methylene blue solution. The charcoal farther back in the tubes had not changed appreciably in appearance or activity. It was thought from this that a certain amount of oxygen from the air might be necessary for the activation of the charcoal. As a further test a tube was heated to the highest temperature obtainable with this apparatus, the unsealed end closed with a stopper, and the heating continued in this manner for 48 hours. The activity of the charcoal remained practically unchanged.

After the charcoal had been heated for 24 hours in the silica tubes it was transferred to silica crucibles with tightly fitting covers. When the crucibles and covers were not close fitting, too much air entered during the heating and the charcoal was entirely burned up during the 24 hours. When they fitted too closely, the charcoal was not activated. Finally, we were able to provide conditions such that satisfactory charcoal was fairly easily produced. A crucible, filled with the charcoal and heated for several days over a protected Meker burner, yielded from $1\frac{1}{2}$ to $2\frac{2}{3}$ the crucible volume of active material. Heating for longer periods gave a more active material but was accompanied by a correspondingly larger consumption of charcoal.

The charcoal so obtained had a soft, velvety-black appearance. When finely ground in an agate mortar and suspended in conductivity water it did not produce in the reaction of the water any change detectable by the sensitive indicators of the Clark and Lubs selection prepared for hydrogen-ion determinations. It was, of course, free from chlorides, and a Kjeldahl determination indicated the absence of combined nitrogen. Ash determinations made on a sample before activation showed 0.0002 g. in 3.0486 g. of charcoal; after activation 2.7686 g. gave 0.0003 g. of ash.

Work of Other Investigators

Many attempts have been made to answer the question as to whether or not adsorption by charcoal results in decomposition of an electrolyte so that either an acid or a base is set free in solution.

In this connection the work of Freundlich⁶ and of Michaelis⁷ and their co-workers has been referred to more frequently than that of any others in recent years. Their earlier researches were put forth to substantiate the theory that the ions of an electrolyte are not adsorbed in equivalent amounts with the result that the solution was left either acid or alkaline in reaction. Recently Michaelis and Rona^{7,8} have repeated some of their earlier work on adsorption and have come to the opposite conclusion, namely, that the ions of an electrolyte are adsorbed in equivalent quantities and that the hydrolytic adsorption of one or the other ion does not take place. Odén and Andersson⁹ also have recently presented data to show that adsorption is equivalent and they maintain that a so-called "decomposition" adsorption is only apparent.

It is worth while at this point to note that all these investigators used the same kind of adsorbent, namely; Merck's blood charcoal. In some cases the preparation was used without any attempt at purification; in others, attempts were made to remove the acid-soluble material.

Freundlich and Losev repeatedly boiled the charcoal with conc. hydrochloric acid. By this process the ash content was reduced from 8% before treatment to 5-7% after treatment.

Odén and Andersson used the same method of extraction but dried their preparation at 125°.

Michaelis and Rona used blood charcoal without any attempt at purification. They were aware that their material was far from ideal for the purpose but stated that a sample of cane sugar charcoal prepared by them could not be reduced finely enough, mechanically, to give sufficient adsorption.

When the process of carbonization of animal matter is studied and the possibility of mechanical occlusion considered, it is not difficult to understand why it is impossible to effect any considerable degree of purification of such charcoal by subsequent treatment with acid. The following experiment illustrates this point rather convincingly and also shows what may be expected from commercial charcoal. A sample of sugar charcoal purchased on the open market gave an acid extract upon treatment with water. Burning off the carbon left a brown ash which was almost completely soluble in hydrochloric acid and which was to all appearances largely iron. A portion of this charcoal was repeatedly boiled with conc. hydrochloric acid until no more iron could be detected in the filtrate. It was then thoroughly washed and an ash determination again made. This ash was almost completely soluble in hydrochloric acid and carried a large amount of iron. Determination of ash in 4.7846 g. of the charcoal before extraction gave 0.0288 g. or 0.57%; and after extraction the same weight of charcoal gave 0.0263 g. of ash or 0.55%. This experiment shows clearly the difficulty of purifying commercial sugar charcoal by acid treatment.

Adsorption of Dyes

Organic acid and basic dyes of the electrolyte type, because of their

⁶ Freundlich and Losev, *Z. physik. Chem.*, **59**, 284 (1907).

⁷ Michaelis and Rona, *Biochem. Z.*, **97**, 57 (1919).

⁸ Rona and Michaelis, *ibid.*, **103**, 19 (1920).

⁹ Odén and Andersson, *J. Phys. Chem.*, **25**, 311 (1921).

high adsorbability, have proved to be nearly ideal substances for use in a study of adsorption of electrolytes by charcoal. They have the disadvantage that they are with difficulty produced in a state of high purity.

In beginning the study of the nature of adsorption by activated sugar charcoal we deemed it advisable to see how this product compared in its behavior toward dyes with the animal charcoal used by Michaelis and Rona. Its action toward methylene blue, a basic dye of the electrolyte type whose cation is an organic radical and whose anion is chlorine, was first investigated. The purity of the methylene blue preparation was found to be approximately the same as that used by them. A 0.0025 *M* solution gave a Sørensen value of P_H 4.02, whereas their 0.002 *M* solution gave P_H 4.26. A sample of 1.0005 g. was charred and ignited with conc. sulfuric acid. A residue of 0.0022 g. of ash, or 0.22%, compared favorably with their 0.17% ash. The solution of the ash and the dye solution both gave a strong flame test for sodium. The preparation evidently contained as an impurity a small amount of sodium chloride and was in this respect also very similar to theirs.

Since the state of combination of the chlorine after adsorption determines whether or not the adsorption of methylene blue is equivalent or hydrolytic in its nature, a solution of methylene blue, 0.0025 *M* with respect to its chlorine content was prepared. The chlorine was determined by dissolving the methylene blue in conc. sulfuric acid and collecting the evolved hydrogen chloride in standard silver nitrate solution. This displacement was accomplished by aeration with an ammonia and carbon dioxide-free stream of air, using a somewhat modified form of apparatus described by Weiser and Sherrick.¹⁰ It was found that 0.3197 g. of methylene blue required 4.98 cc. of 0.02 *N* silver nitrate solution (average of 4 samples), whereas the calculated amount was 5.00 cc.

The proper amount of methylene blue was then used in making up the 0.0025 *M* solution. The chlorine in an aliquot of this solution was determined in the same way. Twenty-five cc. of this 0.0025 *M* methylene blue solution required 3.16 cc. of 0.02 *N* silver nitrate solution, whereas the calculated amount was 3.13 cc.

The decolorizing action of a number of charcoals using this methylene blue solution was then studied. Particular attention was given to the reaction of the decolorized solution after adsorption.

Results with Animal Charcoal

Two samples of animal charcoal obtained from different sources were used. The general results obtained with them were similar, as is shown below.

Acidity of Water Extract of Animal Charcoal No. 1.—Samples of charcoal of 2 g. each were suspended in 50 cc. of water and allowed to

¹⁰ Weiser and Sherrick, *J. Phys. Chem.*, **23**, 205 (1919).

stand for 3 hours with frequent shaking. They were then filtered, and washed, and the amount of acid set free determined by titration with 0.02 *N* sodium hydroxide solution, using methyl red as indicator. The amount of acid set free both with and without methylene blue is indicated below.

TABLE I
ACIDITY OF SOLUTION AFTER ADSORPTION WITH CHARCOAL 1
Amount of charcoal: 2 g.

Water used	0.0025 <i>M</i> methylene blue added	0.02 <i>N</i> acid set free
Cc.	Cc.	Cc.
50	..	0.15
50	..	0.15
..	16	0.75
..	16	0.80

The larger amount of acid is set free when methylene blue is present.

Acidity of Water Extract from Animal Charcoal No. 2.—Experiments similar to those with Charcoal 1 were carried out.

TABLE II
ACIDITY OF SOLUTION AFTER ADSORPTION WITH CHARCOAL 2
Amount of charcoal: 0.5 g.

Expt.	Water used	0.0025 <i>M</i> methylene blue added	0.02 <i>N</i> NaOH added	0.02 <i>N</i> acid set free
	Cc.	Cc.	Cc.	Cc.
1	50	..	..	0.15
2	..	50	..	3.75
3	..	25	..	1.65
4	..	50	..	3.60
5	..	50	3.60	1.70

From Tables I and II it is noted that the adsorption of methylene blue by acid animal charcoals results in setting free considerable amounts of acid. Also, even though enough alkali was added before adsorption to this solution to neutralize the acid set free by these amounts of charcoal and methylene blue, it did not prevent setting free a considerable amount of acid. This is shown in Expts. 4 and 5. Qualitative tests for chlorides were made on the solutions after decolorization of methylene blue and in all cases it was found that fairly large amounts were present.

The commercial sugar charcoal which we have previously described in connection with the extraction with hydrochloric acid, before activation, gave an acid water extract and was entirely devoid of any decolorizing

Commercial sugar charcoal	Treatment	0.02 <i>N</i> HCl required
G.		Cc.
1.0	Boiled with water and filtered	2.00
0.5	+ 50 cc. cold water and filtered	2.00
0.5	+ 16 cc. 0.0025 <i>M</i> methylene blue	0.20
0.5	+ 16 cc. 0.0025 <i>M</i> methylene blue	0.30

power for the methylene blue solution. After activation its water extract was strongly alkaline. The activated material gave the preceding results.

Samples of activated coconut charcoal and activated sugar charcoal prepared from beet sugar which had not been recrystallized also gave aqueous extracts that were strongly alkaline. When methylene blue solutions were decolorized by these charcoals the resultant solutions were alkaline but less so than the aqueous extract of the same amount of charcoal.

Adsorption with Ash-Free Carbon

The decolorizing action of the ash-free, activated sugar charcoal on methylene blue solution was studied under the same conditions as those chosen by Michaelis and Rona in their work with animal charcoal. They found that when methylene blue solutions were completely decolorized by animal charcoal the resulting solution was neutral or faintly alkaline and from 5.5 to 35% of the chlorine of the methylene blue remained in solution as neutral chlorides. They concluded from this and from similar data obtained with other basic and acid dyes that adsorption is equivalent and that in no case was there any indication of hydrolytic adsorption with the resultant setting free of acid or alkali. The appearance of calcium and other chlorides in solution was easily accounted for by the presence of these bases as impurities in their charcoal.

Provided ash-free, activated sugar charcoal were to behave in a similar manner it should be found that there is only equivalent adsorption of methylene blue. The filtrate after decolorization should be neutral and there should be no chlorides in solution. In our work these expectations were only partially fulfilled. The filtrates were found to be absolutely neutral. It was somewhat surprising, however, to find a small amount of chloride in these neutral filtrates. The method of preparation of the charcoal precluded the possibility of any contamination by neutral chlorides and the only source of the neutral chlorides remaining was the methylene blue. As stated before, the methylene blue contained sodium chloride as an impurity. Further evidence indicating this as the source of the neutral chloride will appear later.

A number of samples of the ash-free, activated charcoal were tested as follows.

The charcoal, finely ground in an agate mortar, was placed in small Erlenmeyer flasks, the methylene blue solution added, and the flasks evacuated for a few minutes with a good water pump to remove as much of the occluded air as possible in order to allow better contact with the methylene blue solution. The suspension was allowed to stand, with occasional shaking, for a length of time sufficient for complete decolorization. The charcoal was then filtered off through a small disc of ash-free filter paper in a 30cc. Gooch crucible and repeatedly washed. The reaction of the filtrate was tested and the amount of chloride present determined by concentrating the filtrate and washings to a volume of approximately 10 cc. and titrating with 0.02 *N* silver nitrate solution, using potassium chromate as indicator.

TABLE III
 ADSORPTION OF METHYLENE BLUE BY CHARCOAL

Using a small amount of methylene blue		
Charcoal	0.0025 <i>M</i> methylene blue	0.02 <i>N</i> AgNO ₃ required
G.	Cc.	Cc.
0.25	16	0.24
1.00	50	0.60
1.00	50	0.56
0.25	56	0.47
0.25	16	0.10
0.25	16	0.24

In every instance the filtrate was colorless, neutral, and contained a small amount of neutral chloride. These data seemed to confirm the results obtained by Michaelis and Rona and seemed to substantiate their statement that hydrochloric acid is not set free under these conditions.

Since the methylene blue in solution is hydrolyzed to a certain extent, there are present in addition to the methylene blue molecules and the ions resulting from its dissociation, also methylene blue hydroxide and hydrochloric acid. The above data give no clue to the manner in which all these are removed from solution. The methylene blue molecules alone might be adsorbed, thus causing the eventual complete association of the ions and the reaction of the hydrolytic products. The hydrolytic products might be adsorbed with the result that all of the methylene blue would be hydrolyzed. Another possibility is that the methylene blue molecules, the methylene blue hydroxide molecules, and the hydrochloric acid molecules might all be adsorbed. This would result in complete adsorption of all solutes present.

It was found that the charcoal, after adsorption of methylene blue under the above conditions, was still able to take up a considerable quantity of hydrochloric acid. This was shown by the following two experiments.

1. Two g. of charcoal, after completely decolorizing 80 cc. of 0.0025 *M* methylene blue solution, took up 12.11 cc. of 0.02 *N* hydrochloric acid. 2. To a mixture of 58 cc. of 0.0025 *M* methylene blue solution and 2.00 cc. of 0.02 *N* hydrochloric acid sufficient charcoal was added to decolorize the solution completely. The charcoal was filtered off and washed. In the filtrate was found 0.20 cc. of 0.02 *N* hydrochloric acid.

These results immediately suggested the possibility that, if the charcoal were more nearly saturated with methylene blue, there might be set free either acid or base. This, proved to be the case as shown by the data following in Table IV.

To a given weight of charcoal was added sufficient methylene blue solution so that at the end of a day or two there still remained in solution a small amount of color equivalent to about 0.05 cc. of 0.0025 *M* methylene blue. The charcoal was then filtered off in the usual way and the acid and chloride content of the filtrate determined.

TABLE IV
ADSORPTION OF METHYLENE BLUE BY CHARCOAL
Using a large amount of methylene blue

Charcoal taken	0.0025 <i>M</i> methylene blue added	0.02 <i>N</i> NaOH required to neutralize filtrate	0.02 <i>N</i> AgNO ₃ required by filtrate
G.	Cc.	Cc.	Cc.
0.30	160	3.32	5.38
0.25	100	3.72	4.50
0.25	100	3.22	3.73

Here, indeed, was evidence of a hydrolytic adsorption. It appeared probable that the methylene blue hydroxide was adsorbed to a greater extent than the hydrochloric acid. In order to study this action more closely, the following experiment was performed.

0.25 G. samples of charcoals of different degrees of activity were treated with successive portions of 16 cc. of 0.0025 *M* methylene blue solution. The charcoal was filtered off and washed after each addition of methylene blue and the amount of acid and chlorine in the filtrate determined. *This procedure was repeated until the charcoal no longer decolorized the solution sufficiently for the determinations to be made on the filtrate.* In the case of Charcoal 3 the second addition was 64 instead of 16 cc. of 0.0025 *M* methylene blue. Charcoal 5, before the addition of the first 16 cc. of methylene blue solution, had been treated with hydrochloric acid by suspending it for 24 hours in 10.17 cc. of 0.02 *N* hydrochloric acid. It was then centrifuged and 5.0 cc. pipetted off, titrated with 0.02 *N* sodium hydroxide solution (3.02 cc. required), and the chloride determined by titration with 0.02 *N* silver nitrate solution (3.03 cc.). The charcoal was filtered from the remainder of the solution, the filtrate and washings were also titrated with 0.02 *N* sodium hydroxide solution (2.97 cc.), and chloride determination made (3.10 cc. of silver nitrate solution required). The charcoal, therefore, carried 4.18 cc. of 0.02 *N* hydrochloric acid before it was used to adsorb the methylene blue.

The data for the 5 charcoals are given in Table V.

TABLE V
HYDROLYTIC ADSORPTION OF METHYLENE BLUE

Successive additions of 16 cc. of methylene blue and amounts of reagents required in titrations

Char-coal	0.02 <i>N</i> solution	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th
1	NaOH, cc.	0.00	0.00	0.00	0.20	0.30	0.40	0.45	..	..	..
	AgNO ₃ , cc.	0.19	0.19	0.32	0.53	0.71	0.69	0.91	..	..	..
2	NaOH, cc.	0.00	0.00	0.00	0.30	0.30	0.40	0.45	0.45	0.50	0.55
	AgNO ₃ , cc.	0.23	0.35	0.18	0.54	0.66	0.62	0.72	0.76	0.95	0.90
3	NaOH, cc.	0.00	2nd Addition			0.70	0.45	0.55	..	..	..
	AgNO ₃ , cc.	0.19	64 cc. of 0.0025 <i>M</i>			1.64	0.91	0.86	..	..	..
4	NaOH, cc.	0.00	0.05	0.20	0.75	0.45	0.65	..	..	..	..
	AgNO ₃ , cc.	0.24	0.34	0.54	0.87	0.91	1.10	..	..	..	..
5	NaOH, cc.	1.11	1.15	1.02	1.07	..	..	..	..	..	..
	AgNO ₃ , cc.	1.41	1.43	1.31	1.44	..	..	..	..	..	..

It is clearly shown by the data in this table that (1) up to a certain amount, the adsorption of methylene blue or its hydrolytic products is

complete or equivalent, but beyond that amount free hydrochloric acid remains in solution; (2) when the charcoal is first treated with hydrochloric acid and then washed until no more acid is removed, it is still capable of decolorizing methylene blue solution (four 16cc. additions were made) but hydrochloric acid remains in the solution; (3) the small but definite amount of neutral chloride (0.2–0.3 cc. of 0.02 *N* per 16 cc. of 0.0025 *M* methylene blue) remaining after adsorption comes, as previously stated, from the sodium chloride in the methylene blue.

Further evidence that the sodium chloride remains in solution under these conditions is shown by the data obtained in the following experiments.

To a solution containing 16 cc. of 0.0025 *M* methylene blue and 1.02 cc. of 0.02 *N* sodium chloride solution was added 0.25 g. of the charcoal. After the solution had been completely decolorized the charcoal was filtered off and washed. The filtrate was neutral and required 1.21 cc. of 0.02 *N* silver nitrate solution. Thus it is seen that all of the 1.02 cc. of added chloride, together with 0.19 cc. in addition, which must have come from the methylene blue solution, remained in solution after the adsorption of the methylene blue. The same charcoal was again suspended in 16 cc. of 0.0025 *M* methylene blue solution, but this time without the addition of any sodium chloride. After complete decolorization the filtrate was found to be neutral and contained 0.20 cc. of 0.02 neutral chloride solution.

Neutralization of Sodium Hydroxide by Adsorbed Methylene Blue

When activated, ash-free sugar charcoal that has adsorbed a known amount of methylene blue is suspended in sodium hydroxide solution, the sodium hydroxide is neutralized and there appears in solution an amount of sodium chloride equivalent to the chloride originally held by the charcoal. No trace of color, however, is imparted to the solution by this treatment. At room temperature it requires a considerable length of time with shaking, or a number of extractions with 0.02 *N* sodium hydroxide solution, to remove all the chloride from the charcoal. Boiling for a few minutes

TABLE VI
NEUTRALIZATION OF SODIUM HYDROXIDE BY ADSORBED METHYLENE BLUE

Expt.	Char-coal G.	Extractions with NaOH	Period of contact of NaOH with adsorbent	0.02 <i>N</i> NaOH used in each extraction Cc.	0.02 <i>N</i> chlor- ide originally adsorbed on the charcoal Cc.	0.02 <i>N</i> chloride removed by the extractions Cc.
1 ^a	1.0	3	10 days	10.00	5.69	5.55
2 ^a	1.0	2	9 days	10.00	8.13	6.33
3 ^a	0.25	1	3 hrs.	5.04	1.90	1.39
4 ^b	0.25	1	10 min.	14.10	10.46	11.07
5 ^b	0.25	1	10 min.	20.14	14.09	14.45
6 ^b	0.30	1	10 min.	20.14	14.62	15.01
7 ^a	0.25	2	1 day	5.04	1.76	1.72

^a Room temperature.

^b Boiling temperature.

seems to remove it completely. An exhaustive investigation of the conditions for the removal of the adsorbed chloride such as the amount of shaking, period of contact, and temperature was not made and the preceding data are presented merely to indicate the general trend of the action.

In connection with this table it is noteworthy that Expts. 4 and 5 were performed using Charcoals 1 and 2, respectively, of Table V. After adsorption of methylene blue with the results given in Table V these charcoals were suspended in water and the stated amounts of 0.02 *N* sodium hydroxide solution added, after which the solutions were boiled for about 10 minutes. They were then filtered and the chloride in the filtrate determined. With this information at hand all the chlorine originally contained in the methylene blue solutions used in these two cases is accounted for.

Summed up in terms of 0.02 *N* solutions it is as follows.

	Charcoal	
	4	5
	Cc.	Cc.
HCl set free during adsorption.....	1.15	2.95
Neutral chloride in solution after adsorption.....	2.39	2.96
NaCl formed by boiling with 0.02 <i>N</i> NaOH.....	11.07	14.45
Chloride accounted for.....	14.61	20.36
Chloride in the methylene blue (calc.) decolorized.....	14.00	20.00

If, to a methylene blue solution an amount of sodium hydroxide equivalent to, or slightly in excess of, that necessary to combine with the chlorine of the methylene blue (assuming it is set free as hydrochloric acid during adsorption) be added and the solution decolorized with the activated charcoal, it is found that the chlorine of the methylene blue remains quantitatively in solution as sodium chloride and that the sodium hydroxide has been neutralized. The data in the following table show clearly that this is what happens.

TABLE VII
SELECTIVE ADSORPTION OF METHYLENE BLUE HYDROXIDE

0.25 g. of charcoal used			
0.02 <i>N</i> NaOH added Cc.	0.0025 <i>M</i> methylene blue decolorized Cc.	0.02 <i>N</i> NaCl possible Cc.	0.02 <i>N</i> NaCl found Cc.
16.17	128.00	16.00	15.53
7.05	50.00	6.25	5.95
7.05	50.00	6.25	5.90
7.05	50.00	6.25	6.00

From the above data it would be anticipated that if a methylene blue solution were decolorized by a blood charcoal that gives an alkaline extract with water, there would, after adsorption, be more or less neutral

chloride remaining in solution, the amount depending of course upon the amount of base available in the charcoal. Under these conditions it would be impossible to detect any hydrolytic adsorption with the corresponding liberation of hydrochloric acid, because the free acid would be immediately neutralized. This clearly accounts for the fact that Michaelis and Rona⁶ did not detect any free hydrochloric acid in those cases in which their charcoal was not used in excess and their solutions were not completely decolorized. This also explains why they found as high as 35% of the chlorine of methylene blue remaining in solution as neutral chloride.

Still another point which is opposed to the theory that hydrolytic adsorption does not exist is the fact that even during the process of adsorption of small amounts of methylene blue there actually exists in solution much free hydrochloric acid. Evidently the methylene blue hydroxide is taken up more rapidly than the hydrochloric acid, although at the end of the adsorption it is found that both have been completely removed from solution. Experiments were carried out using 0.25 g. samples of activated charcoal such as easily decolorized 48 cc. of 0.0025 *M* methylene blue solution and left the solution neutral. When the charcoal was filtered off quickly with suction while the solution was still deeply colored it was found that there was in the filtrate as much as 0.6 cc. of 0.02 *N* hydrochloric acid. When the charcoal was again suspended in this same filtrate and the decolorization allowed to go on to completion after which the charcoal was again filtered off, the filtrate was found to be neutral. There may be several explanations for this action but the simplest, and perhaps the most logical one is that the charcoal adsorbs, at different rates, the methylene blue hydroxide and hydrochloric acid molecules resulting from the hydrolysis of methylene blue. The adsorption of the hydrolytic products that are already present in solution before the charcoal is added would result in the hydrolysis of additional methylene blue molecules. If the rate of adsorption of the methylene blue hydroxide were greater than that of the hydrochloric acid, there would be an excess of hydrochloric acid present. The facts seem to substantiate this view.

Results with Acid Treated Charcoals

The widely differing and apparently erratic results obtained in the adsorption of basic dyes by treated charcoals becomes somewhat clearer after a study of adsorption of such dyes by acid treated, ash-free sugar charcoal. When ash-free, activated charcoal is suspended in an excess of 0.02 *N* hydrochloric acid considerable amounts of the acid are adsorbed and cannot be washed out with cold water. By the use of sufficient charcoal an acid solution is so completely freed from acid that not a trace, detectable by sensitive indicators, remains. If this charcoal, carrying adsorbed acid, is used to decolorize methylene blue solution, hydrochloric

acid is immediately set free and is not subsequently removed from solution. The following experiment will illustrate this point. A number of samples of ash-free charcoals were suspended in known amounts of 0.02 *N* hydrochloric acid for varying periods of time; all were then washed until no more acid could be detected in the filtrate and washings and each sample was treated with 0.0025 *M* methylene blue solution. The amounts of charcoal used, adsorbed acid, methylene blue solution used, and acid remaining in solution after decolorization are given in the following table.

TABLE VIII
ADSORPTION OF METHYLENE BLUE BY ACID TREATED CHARCOAL

Charcoal G.	0.02 <i>N</i> HCl adsorbed Cc.	0.0025 <i>M</i> methylene blue solution decolorized Cc.	0.02 <i>N</i> HCl left in solution Cc.
1.00	9.73	50.00	2.80
1.00	9.58	50.00	3.00
0.25	4.17	64.00	4.35
0.25	2.72	24.00	1.25

It is thus seen that the results of adsorption of methylene blue by acid-treated, ash-free sugar charcoals are, in some respects, the exact opposite of those obtained with the untreated material. In all cases in the above table the same weight of untreated charcoal, that is, charcoal free from adsorbed acids, would have decolorized the solutions, leaving them strictly neutral. The conclusion drawn from results obtained from the adsorption of basic dyes by acid-extracted charcoals, supposedly washed free from acid, would naturally be that the adsorption is entirely hydrolytic since, as shown in the case of Charcoal 5 of Table V, the adsorption of even small amounts of methylene blue results in an acid solution instead of a neutral one. This is exactly the conclusion that Freundlich and Losev⁵ held after using the acid treated charcoals prepared as described earlier in this paper. Using blood charcoal and sugar charcoal, washed until the filtrates were free from acid and chlorides, they studied the adsorption of crystal violet, a basic dye of the same type as methylene blue. They found that the adsorption of this dye resulted in the setting free of hydrochloric acid and came to the conclusion that the adsorption of basic dyes by charcoal is accompanied by the setting free of hydrochloric acid which "remains quantitatively in solution as such." This conclusion was hardly justified in view of the fact that they tested the reaction of the decolorized solution with litmus paper and then determined the chloride content quantitatively and assumed that it was all present in the form of hydrochloric acid.

In order to confirm our own views further, a 0.0025 *M* solution of crystal violet was prepared and small amounts were decolorized with un-

treated ash-free, activated sugar charcoal. The resulting solution was found, as expected, to be strictly neutral. With larger amounts of the crystal violet some hydrochloric acid remained in solution.

At this point it may be well to include results of one experiment in which an activated, ash-free sugar charcoal apparently gave a hydrolytic adsorption with small amounts of methylene blue. A sample of ignited, ash-free charcoal was heated in a shallow, uncovered platinum dish in an attempt to activate it at a low temperature. The charcoal was repeatedly heated to incipient redness over a free flame from a Meker burner and, as it cooled, was stirred to bring it in contact with air. This process produced an active, ash-free charcoal that decolorized methylene blue solutions readily but always with the liberation of hydrochloric acid. Another sample was activated in a silica dish in the same manner and acted in the same way. This was opposed to all the results so far obtained. Upon investigation it was found that the water suspension of this charcoal was acid. The charcoal had evidently adsorbed acid gases from the burner, for when this acid charcoal was removed and heated to a high temperature in silica tubes, excluding the possibility of such contamination, the adsorbed acid gases were driven off and the charcoal was again neutral in water, and no longer left acid in solutions when small amounts of methylene blue solutions were completely decolorized.

Discussion

Nearly all of our present theories relating to the adsorption of electrolytes from solution by charcoal are based upon results of researches which have been carried out with animal or blood charcoal as adsorbents. Although it has been recognized that these are of complex composition and that no two samples from different sources may be identical either in composition or behavior, the results obtained by their use have been employed in making generalizations and formulations in which the assumption was tacitly made that no complicating factors were in operation.

In the present investigation we wished to obtain a pure type of amorphous carbon, one with a minimum of ash and nitrogen, and one which would lend itself readily to activation. The difficulty of removing the last traces of hydrogen and oxygen from charcoal has been reviewed by Bancroft¹¹ and it is unnecessary to repeat it here.

It seems probable that activation effected by prolonged heating at a temperature somewhat above 1000° would result in either oxidation or vaporization of practically all the hydrogen or hydrocarbons present.

If the activated charcoal be permitted to cool down without the complete exclusion of air, there will result some oxidation, also some subsequent adsorption of carbon dioxide together with oxygen and nitrogen. It

¹¹ Bancroft, *J. Phys. Chem.*, **24**, 127 (1920).

seems very improbable, however, that these were factors of any appreciable importance in connection with the results obtained in this investigation. Care was taken to allow the charcoal to come to room temperature before fully exposing to the air, thereby preventing much oxidation and the adsorption of large amounts of carbon dioxide. As previously mentioned, when the charcoal was suspended in water in a flask and the flask evacuated, a small amount of gas could be withdrawn from the charcoal. A test showed no carbon dioxide; furthermore, removal of the gas from the carbon made no observable difference in the results.

In the light of the data presented in this paper, it seems extremely probable that the statement made by Odén and Andersson⁸ that "the so-called decomposition by adsorption is only apparent, the cause being adsorbed impurities (H or OH ions) which are partially thrown out by the adsorbed solution," does not hold true in the case of adsorption by pure activated, ash-free sugar charcoal. It does, however, hold true in those cases in which the charcoal is first "purified" by treatment with acids or bases and it is, as stated by them, "a striking fact with regard to these researches that those adsorbents which are said to adsorb the base and set the acid free are derived from acid solutions or have been treated with acids, whereas the adsorbents which appear to adsorb the acid and set the base free are prepared from alkaline solutions.

"This can hardly be due to chance only, but depends, on the contrary, on the circumstance that the disintegrated constituent which is said to be set free, is in reality retained as traces of acid or base, not washed out, and not detected until thrown out by the addition of neutral salt solution."

To these considerations may be added the effect of impurities in the adsorbent such as ash contained in animal charcoal. This ash cannot all be removed from the charcoal by extraction with acids and the adsorbed acids in turn cannot be readily removed by washing with water. Re-igniting the charcoal removes the acid but leaves the charcoal alkaline in reaction as in the beginning.

If there can be any doubt remaining that there is hydrolysis or decomposition when activated sugar charcoal adsorbs basic dyes, this doubt must become even more remote when facts mentioned below are considered. It will be shown in another paper that this same charcoal that sets free acid from basic dyes, adsorbs acid dyes with the liberation of free base. Were we to consider the theory that adsorbed hydrogen or hydroxyl ions cause the decomposition to be only apparent it is difficult to see what the origin of this acid and of this base would be in the case of activated, ash-free sugar charcoal, inasmuch as neither carbon dioxide nor ammonia was detected in the adsorption experiments and combined nitrogen was proved to be absent by the Kjeldahl determination. In view of the magnitude of the decomposition of the adsorbed substances and the method of

preparation of the charcoal, it seems that we have precluded the possibility of the cause being adsorbed acids and bases.

It seems logical to assume, therefore, that decomposition or hydrolysis of methylene blue results when a water solution of it is treated with activated, ash-free charcoal and that the products of hydrolysis, namely, methylene blue hydroxide and hydrochloric acid are, up to a certain point, both adsorbed, although at different rates. Beyond this point methylene blue hydroxide is adsorbed to a greater extent than hydrochloric acid and some hydrochloric acid remains in solution.

This process of preferential adsorption may be regarded as a general phenomenon, differing only in degree for different systems.

Adsorption of Acid Dyes by Activated Sugar Charcoal

The acid dyes used were sodium and ammonium picrates and the sodium and ammonium salts of eosin. The sodium and ammonium eosins were used in solutions 0.0025 *M* and the picrates in solutions 0.005 *M*, to correspond with those used by Michaelis and Rona.¹²

Preliminary tests with sodium eosin solution and activated sugar charcoal indicated that the adsorption was accompanied by considerable hydrolysis.

These results were obtained under conditions which precluded the origin of the free base from being any other than the sodium in the sodium eosin. The source of the free base remaining in solution after decoloration could not have been the charcoal for it carried only a few hundredths of a per cent. of ash, was nitrogen-free and, moreover, was sufficiently active so that it was necessary to use only 0.25 g. or less to secure satisfactory results.

It is apparent that it was the conditions under which Michaelis and Rona worked that prevented them from attributing, with certainty, the alkalinity of their decolorized solutions to decomposition of the adsorbed acid dye. Their charcoal contained 7–8% of ash and gave a water extract, the Sørensen value of which was P_H 8.0. The Sørensen value of their potassium eosin solution was P_H 7.11 and of the filtrate after adsorption 8.59, and they were justified, therefore, in concluding that the alkalinity was due to the impurities in the charcoal.

Hydrolytic Adsorption of Acid Dyes

With the information derived from these preliminary experiments at hand, it was deemed desirable to study more closely the adsorption of acid dyes by activated ash-free sugar charcoal, in order to see how this type of adsorption compared with that of the basic dyes, methylene blue and crystal violet. Accordingly, samples of charcoal of 0.25 g. each were placed in 100cc. Erlenmeyer flasks and the stated amounts of the dye solutions added. The flasks were evacuated with a good water pump to re-

¹² Michaelis and Rona, *Biochem. Z.*, **97**, 57 (1919).

move as much as possible of the adsorbed air from the charcoal, vigorously shaken for half an hour, and then allowed to stand for approximately 15 hours with occasional shaking. The charcoal was then filtered off with suction through a small disc of ash-free filter paper in a 25cc. Gooch crucible and the alkali in the filtrate determined by titration with 0.02 *N* hydrochloric acid, using phenol red as indicator. The charcoal was returned to the flask and the next addition of solution made. This procedure was repeated until the solutions were no longer sufficiently decolorized to permit accurate titrations to be made. The results are summarized in Table IX.

TABLE IX
HYDROLYTIC ADSORPTION OF ACID DYES

Amount and conc. of each addition Cc.	Cc. of 0.02 <i>N</i> alkali set free with each successive addition of solution					
	1st	2nd	3rd	4th	5th	6th
0.005 <i>M</i> sodium picrate						
5	0.95	0.75	0.45	0.25	0.05	0.05
5	1.00	.75	.40	.25	.07	.05
15	2.00	.65	.20	.05	..	..
20	2.15	.60	.10	.05	..	..
25	2.10	.50	.10	.05	..	..
25	2.30	.55	.10	.05	..	..
50	2.55	.35	.10	.05	..	..
50	2.60	.30	.05	..	..	..
0.005 <i>M</i> ammonium picrate						
5	0.80	0.70	0.40	0.20	0.05	0.05
5	1.10	.80	.60	.20	.10	.05
25	2.10	.35	.10	.00	.05	..
25	2.45	.40	.10	.05	..	..
50	2.50	.35	..	..	..	..
50	2.75	.35	0.05	..	..	..
0.0025 <i>M</i> sodium eosin						
10	0.75	0.35	0.30	0.20	..	..
25	1.10	.35	.40	.20	..	..
50	1.25	.20	.10	.05	..	..
0.0025 <i>M</i> ammonium eosin						
10	0.70	0.35	0.20	0.15	..	..
25	1.50	.40	.30	.15	..	..
50	1.75	.30	.20	.05	..	..

A glance at Table I reveals the striking fact that in the adsorption of acid dyes the greater amounts of alkali are set free when the first additions of the solutions are decolorized, the amount set free diminishing rapidly with successive additions of solution and with decrease in adsorption.

This is just the reverse of the order in which acid is set free during the adsorption of the basic dyes, methylene blue and crystal violet. With successive additions of 16 cc. of 0.0025 *M* methylene blue solution to 0.25

g. of charcoal, the first 2 or 3 additions were completely decolorized, leaving the solutions neutral, while each subsequent addition was decolorized to a less degree and the resulting solution contained increasingly greater amounts of hydrochloric acid. It was also found that from a mixture of small amounts of the methylene blue solution and hydrochloric acid charcoal adsorbed both the solutes and left the solution neutral. Parallel experiments with acid dyes and sodium hydroxide were carried out by decolorizing the dye solutions alone and in the presence of known amounts of sodium hydroxide and determining the amount of sodium hydroxide remaining in solution after complete removal of the color.

It was found that the presence of a small amount of added alkali had no appreciable effect on the amount of base set free during adsorption from the solution of acid dye. These results also offer further evidence that, whereas activated ash-free sugar charcoal will decolorize certain amounts of the basic dyes, methylene blue and crystal violet, leaving the solutions neutral and still have the power to take up certain amounts of acids, it decolorizes solutions of the acid dyes, *but in this case leaves the resulting solutions alkaline and does not have the power of taking up the base set free by hydrolysis of the acid dye in solution.*

At first thought these results may seem somewhat surprising. Reasoning from the behavior of basic dyes, which in small amounts were completely adsorbed, it might have been expected that the adsorption of small amounts of acid dyes would likewise result in a neutral solution and that the adsorption of larger amounts would leave the solution alkaline. A consideration of the theory of hydrolytic adsorption of dyes, and of the fact that in general charcoal adsorbs either organic or inorganic acids far more readily than inorganic bases, gives us at once a simple and satisfactory explanation for the preceding results; and it will be seen that the foregoing data, obtained in the study of adsorption of acid and basic dyes by activated ash-free sugar charcoal, are convincing evidence in support of this hydrolytic adsorption theory.

Relative Adsorption of Acids and Bases

Before taking up in detail a discussion of the data and theory it is necessary to consider the relative adsorption of acids and bases by activated sugar charcoal. The adsorption of a number of the more common organic and inorganic acids and inorganic bases by activated ash-free sugar charcoal was determined. In Table X is summarized the amount of acid or base adsorbed by 0.25 g. of the charcoal from 100 cc. of 0.01 *N* solution.

The data in this table indicate the marked selective adsorption by activated, ash-free sugar charcoal for the various groups of acids and bases. It is significant that the organic acids are as a rule adsorbed to a greater extent than inorganic acids. The most striking fact, however, is that

TABLE X
ADSORPTION OF ACIDS AND BASES BY CHARCOAL

Acid or base	Amount of acid or base adsorbed by 0.25 g. of charcoal expressed in cc. of 0.01 <i>N</i> solution	Acid or base	Amount of acid or base adsorbed by 0.25 g. of charcoal expressed in cc. of 0.01 <i>N</i> solution
Group 1. Aromatic acids		Group 4. Inorganic acid	
Benzoic.....	75.80	Hydrochloric.....	11.22
Hydroxybenzoic (salicylic).....	73.76	Perchloric.....	10.86
<i>o</i> -Aminobenzoic (anthranilic)....	67.00	Nitric.....	10.08
Group 2. Dicarboxylic acids		Sulfuric.....	9.66
Succinic.....	48.00	Hydrobromic.....	8.54
Hydroxysuccinic (malic).....	35.88	Group 5. Inorganic hydroxides	
Dihydroxy-succinic (tartaric)....	31.76	Sodium.....	0.10 ^a
Aminosuccinic (aspartic).....	8.78	Potassium.....	0.00
Group 3. Aliphatic acids		Calcium.....	0.00
Formic.....	15.70	Barium.....	0.04 ^b
Acetic.....	16.44	Ammonium.....	0.00
Propionic.....	24.36	Magnesium.....	00.0
Butyric.....	35.52		
Hydroxypropionic (lactic).....	17.86		
Amino-acetic (glycocoll).....	0.0		

^a Nearly saturated solution.

^b These small values are probably due to carbon dioxide.

the strong inorganic bases are not adsorbed at all. In this connection it may be well to point out that, if precautions are not taken to exclude carbon dioxide, results may be obtained which would indicate the adsorption of considerable amounts of these bases. Failure to take this precaution, together with the presence in many charcoals of undetected adsorbed acids, is undoubtedly responsible for the positive values usually assigned to the adsorption of inorganic bases by charcoal. When this property of the charcoal is considered, the results obtained during adsorption of the acid and basic dyes can be easily and satisfactorily explained by accepting the theory of preferential adsorption of either or both the acid and base set free by hydrolysis of the salts in solution.

In the case of methylene blue and crystal violet it was shown that certain amounts were completely adsorbed leaving the solutions neutral, although during the course of adsorption the solutions contained relatively great amounts of acid. The adsorption of still greater amounts of dye left the solutions increasingly acid. In this case both products of hydrolysis, the dye base and hydrochloric acid, were adsorbed although at different rates and to different degrees; the methylene blue hydroxide being taken up more readily than the hydrochloric acid. When small amounts of these dyes are adsorbed the charcoal is still able to take up the hydrochloric acid, but as it reaches its limit of adsorptive capacity more and more of the acid remains in solution.

With the acid dyes the conditions are quite different. The products

of hydrolysis are organic acids and sodium or ammonium hydroxide. The organic acids are strongly adsorbed while the sodium and ammonium hydroxides are not adsorbed at all. The reason is evident, therefore, why in Table IX the larger amounts of alkali appear during the first additions of the acid dye solutions. The base is not adsorbed by the charcoal and remains in solution. It is also evident that the adsorption of acid dyes is not entirely hydrolytic, since only part of the base remains in solution after complete adsorption of the acid. It is probable that a part of the dye is removed as undissociated molecules of the salt.

From the study of the adsorption of basic and acid dyes of the electrolyte type, where in one case the dye is a product of a strongly adsorbed base and a feebly adsorbed acid, and in the other a product of a strongly adsorbed acid and a feebly adsorbed base, and also from a knowledge of the relative adsorbability of the more common acids and bases, it should be possible to predict in a general way what the relative acidic or basic reaction of almost any salt solution would be after treatment with activated ash-free charcoal.

In order to try this out experimentally a number of solutions of various salts were prepared and the reaction before and after treatment with charcoal roughly estimated by means of the indicators of the Clark and Lubs series for hydrogen-ion determinations. The concentration of the solutions was 0.02 *N* except in those cases where the salt was not sufficiently

TABLE XI
CHANGE IN HYDROGEN-ION CONCENTRATION DUE TO ADSORPTION

Solution	P_H before adsorption	P_H after adsorption	Solution	P_H before adsorption	P_H after adsorption
Sodium chloride.....	7.0	9.0	Barium acetate.....	7.2	8.+
Sodium potassium tartrate	7.2	8.6	Calcium acetate.....	7.4	8.4
Sodium citrate.....	7.8	8.8	Magnesium chloride....	6.8	8.0
Sodium salicylate.....	7.0	9.4	Magnesium nitrate....	6.8	8.0
Sodium acetate.....	7.2	8.2	Lead nitrate.....	5.0	6.2
Sodium phosphate (Na_4PO_4)	8.2	8.2	Cadmium chloride....	6.7	7.4
Potassium nitrate.....	6.8	9.4	Manganese sulfate....	4.4	7.4
Potassium chlorate.....	7.0	8.8	Copper acetate.....	4.8	4.8
Potassium bromide.....	7.0	8.6	Zinc sulfate.....	6.8	7.0
Potassium iodide.....	7.0	8.8	Zinc lactate.....	7.0	7.0
Potassium ferrocyanide...	7.0	7.8	Aluminum sulfate....	<4.4	<4.4
Potassium phosphate (KH_2- PO_4).....	4.4	6.6	Ferric chloride.....	<4.4	<4.4
Ammonium bromide.....	5.6	8.4	Mercuric chloride.....	4.4	3.8
Ammonium chloride.....	5.6	8.4	Silver nitrate.....	6.8	4.4
Ammonium sulfate.....	6.8	8.4	Silver sulfate.....	6.8	4.4
Ammonium thiocyanate...	5.5	7.8	Silver acetate.....	7.+	5.0
Ammonium picrate.....	4.4	8.6	Platinic chloride.....	<4.4	<4.4
Barium chloride.....	6.8	8.0	Auric chloride.....	<4.4	<4.4
Barium benzoate.....	7.0	9.0			

soluble. Fifteen cc. (approximately) was shaken with 0.2–0.3 g. of charcoal and the mixture allowed to stand for about $\frac{1}{2}$ hour, filtered and the reaction of the filtrate determined. The Sørensen values of the solutions before and after treatment are recorded in Table XI.

The results in this table agree well with those that would be expected from an *a priori* consideration of the conditions obtaining in each instance. As would be anticipated, solutions of the salts of sodium, potassium, ammonium, barium, calcium and magnesium, after treatment with charcoal were distinctly alkaline. The total amount of alkali found in the solutions after adsorption varied from a few hundredths of a cc. of 0.02 *N* solution in the case of solutions such as sodium chloride to 2 cc. or more of solutions of barium benzoate and sodium salicylate. This, too, is in accord with what would be expected, since sodium chloride is derived from a feebly adsorbed acid and a non-adsorbed base and is hydrolyzed only to a very slight extent, while sodium salicylate, derived from a non-adsorbed base and a very strongly adsorbed acid, is hydrolyzed to a greater extent and consequently should offer ideal conditions for considerable hydrolytic adsorption.

The salts of metals such as lead, cadmium, copper, manganese, iron, aluminum, etc., could not be expected to yield strongly alkaline solutions because they are precipitated by a low concentration of hydroxyl ions. Their solutions would not change greatly in their reactions during adsorption.

Solutions of iron and of the noble metals undergo reduction as well as adsorption. Silver, gold and platinum are apparently quantitatively reduced to the metallic form, while ferric chloride is reduced to ferrous chloride, along with the adsorption of considerable amounts of the iron. When relatively small amounts of solutions of iron, silver, gold and platinum salts are decomposed, both the metal and the acid are completely adsorbed leaving the solution neutral. With larger amounts of the solutions more acid remains in solution, the amount depending upon the salt in question. Thus, under certain conditions, with an excess of the approximately neutral solutions of silver nitrate, silver sulfate, and silver acetate, the solution after adsorption is left acid and contains the equivalent of about 1 cc. of 0.02 *N* acid. Under similar conditions solutions of auric and platinic chlorides contain the equivalent of about 16 cc. of 0.02 *N* acid.

In this connection it is interesting to note that when the charcoal is added to the solutions of the noble metals without certain precautions an evolution of gas results which seems to be in no manner connected with the decomposition of the solute except that it is a displacement of adsorbed or dissolved gas by the substances adsorbed. When a water suspension of the charcoal and the solution of the salt are first boiled to remove the adsorbed and dissolved gases and then mixed, there is no evidence

of any evolution of gas even when the containing vessel is evacuated to a point at which the liquid boils. This evidence is contrary to the theory that carbon dioxide is evolved in the decomposition of these salts.¹³

Adsorption of Substituted Organic Acids

A study of the adsorption of the organic acids listed in Table X reveals the effect on the adsorption produced, by the introduction of hydroxyl and amino groups into benzoic, succinic, acetic and propionic acids. The introduction of these groups, in general, decreases the adsorption of the acid to a more or less marked degree, the amount of the decrease depending upon the nature of the group and the acid in which it is substituted. The introduction of the hydroxyl group produces a smaller effect than the introduction of the amino group (which is far more basic) both in the case of aliphatic and aromatic acids. The effect of each group is much more pronounced when substituted in the aliphatic than in the aromatic acids.

From Table X it is seen that *o*-hydroxybenzoic (salicylic) acid is adsorbed to a slightly less extent than benzoic acid. Hydroxysuccinic (malic) and dihydroxy-succinic (tartaric) acids are adsorbed to a much less extent than succinic acid. Hydroxypropionic (lactic) acid is adsorbed much less than propionic acid.

The effect of the amino group is even more striking. Thus *o*-amino-benzoic (anthranilic) acid is slightly less adsorbed than either benzoic or salicylic acid. Aminosuccinic (aspartic) acid is very much less adsorbed than succinic, malic or tartaric acids. Amino-acetic acid (glycocoll) is not adsorbed at all.

In Group 3 of Table X it is also evident that beginning with formic acid and extending through the fourth member of the homologous series of aliphatic acids there is a marked increase in adsorption of aliphatic acids with increase in molecular weight. In the case of the series succinic, malic, and tartaric acids, where an increase in molecular weight is due to the introduction of hydroxyl groups, adsorption decreases with increase in molecular weight.

Results Obtained by Other Investigators

With the data obtained in the investigation of the nature of adsorption of electrolytes from solution by activated ash-free sugar charcoal at hand, it becomes of interest to compare them with those obtained by various investigators with animal and vegetable charcoals.

The results obtained by the use of activated ash-free sugar charcoal in the adsorption of acid and basic dyes of the electrolyte type have led us to conclusions just the reverse of those of Michaelis and Rona¹² who believe that adsorption is not accompanied by hydrolysis. They maintain that there is but one form of adsorption of organic acid and basic dye salts from

¹³ For a discussion of this theory see Bancroft, *J. Phys. Chem.*, **24**, 361 (1920).

pure water by pure charcoal, that in all cases the anion and cation are removed in equivalent amounts, and that a measurable hydrolytic splitting never results from adsorption. The results with neutral, activated, ash-free sugar charcoal described in this paper seem to indicate that the alkaline impurities in their blood charcoal prevented them from attributing with certainty the presence of alkali in their decolorized acid dye solutions to hydrolytic adsorption of the substance in solution. In their work with blood charcoal and basic dyes two factors prevented them from detecting acid set free. The first was the fact that their charcoal carried alkaline impurities and gave an alkaline water extract. The second was that in some instances they used such large quantities of charcoal that any acid that might have been set free would also have been adsorbed.

Bancroft,¹⁴ in a discussion of selective adsorption of salts by charcoal, cites the results obtained by Liebermann with bone black and a number of salt solutions. Liebermann found that from solutions of barium formate, sodium acetate, ammonium oxalate and sodium potassium tartrate the basic constituents were removed by bone black to a greater extent than the acid ones, thus leaving the solutions acid.

When 0.02 *N* solutions of these salts were prepared and treated with neutral, activated, ash-free sugar charcoal it was found, as would be anticipated from the theory and data presented in this paper, that the solutions left were not acid but, on the contrary, strongly alkaline.

Liebermann reported also that calcium and barium benzoates, sodium chloride, sodium nitrate and sodium sulfate were adsorbed without change in reaction of the solutions. Here again it was found by us that the activated ash-free sugar charcoal adsorbed the acid constituents of the solutes to a greater extent than the basic ones and left the solutions distinctly alkaline in the case of the sodium salts and very strongly alkaline by the case of the barium and calcium benzoate.

In all probability Liebermann's results were due to other constituents than the carbon of the bone black, for we have found that an activated, ash-free sugar charcoal carrying a small amount of adsorbed acid leaves these solutions neutral, the alkali set free by hydrolysis being neutralized by the adsorbed acids already on the charcoal. This also was the result obtained by us when acid dyes were adsorbed by a charcoal carrying small amounts of adsorbed acids. The solutions were left neutral.

From the data presented in this and in the previous paper the conclusion is drawn that hydrolysis accompanies and is a considerable factor in the adsorption of electrolytes, especially the acid and basic dyes, by activated, ash-free sugar charcoal. The contention that this phenomenon is due to impurities in the charcoal does not hold in the case of activated, ash-free

¹⁴ Bancroft, *J. Phys. Chem.*, **24**, 360 (1920). The original appeared in *Sitzungsber. Akad. Wiss. Wien.* **75**, II, 331 (1878) and has not been accessible to the the writers.

sugar charcoal. The method of preparation precludes the possibility of ascribing the effects to impurities such as alkaline inorganic matter, combined nitrogen, and adsorbed hydrogen and hydroxyl ions in the charcoal.

We ascribe many of the contradictory effects described to previous investigators to alkaline impurities or to retained acid or base used in attempts to purify complex animal or vegetable charcoals. This view is made more probable by the fact that these effects can be reproduced by treatment of neutral, ash-free sugar charcoal before use, with acids or bases and then washing until the reagents have apparently all been removed.

If the acidity or alkalinity of the solutions after adsorption by ash-free sugar charcoal were due to the displacement or setting free of acid or base previously adsorbed by the charcoal it would be difficult to explain the fact that the same charcoal sets acid free when treated with basic dyes and sets alkali free when treated with acid dyes. Under these conditions it would be necessary to assume that this charcoal carries simultaneously both adsorbed acid and adsorbed base.

On the basis of our experimental results the most logical explanation for the hydrolytic adsorption of electrolytes by charcoal (which adsorption may constitute but a small part of the whole adsorption) seems to be that the charcoal selectively adsorbs the acid or base set free by hydrolysis of the electrolyte in aqueous solution, thus disturbing the equilibrium and causing further hydrolysis of the dissolved substance.

III. THEORETICAL CONSIDERATIONS

Theory of Hydrolytic Adsorption

The comparatively recent work on crystal structure¹⁵ and the orientation of molecules at liquid surfaces^{16,17} has been so well substantiated by experimental facts that there no longer seems to be any question of the validity of the theories covering these subjects. The experimental data on adsorption of solutes by charcoal conforms well with these theories, on the basis that there exists on the surface of the charcoal "residual valence forces" through the operation of which true adsorption occurs. If the view of Haber and Klemensiewicz¹⁸ relative to the functioning of adsorbed water as a reversible type of hydrogen and hydroxyl electrode is applied to water molecules adsorbed on carbon then the behavior of carbon in aqueous solutions of electrolytes becomes readily explainable. According to Lewis¹⁹ each hydrogen atom in a water molecule has the same

¹⁵ Bragg and Bragg, "X-Rays and Crystal Structure," G. Bell & Sons, Ltd., London, 1918.

^{16,17} Langmuir, *J. Am. Chem. Soc.*, **38**, 2221 (1916); **39**, 1848 (1917); Harkins *et al.* *J. Am. Chem. Soc.*, **39**, 345 (1917); **39**, 541 (1917).

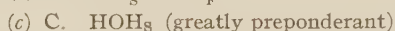
¹⁸ Haber and Klemensiewicz, *Z. physik. Chem.*, **67**, 385 (1909).

¹⁹ Lewis, "Valence and Structure of Atoms and Molecules," Chem. Cat. Co., 1923.

relation to oxygen and the rest of the molecule. If this be true then an adsorbed water molecule might reasonably be supposed to ionize so as to afford either free hydrogen or free hydroxyl ions, each capable of displacement by other ions.

Mechanics of Adsorption

We may consider the following as representing equilibrium conditions of the system, carbon-water.



Where C represents carbon adsorptive capacity, H_s^+ and OH_s^- represent adsorbed ions, H_f^+ and OH_f^- represent "free ions" in liquid layer (outer electrical layer).

With this view it is possible to see that either or both H_s^+ and OH_s^- might be displaced, also that the velocity of the displacement reactions may be far different.

Replacement Effects of Ions with Carbon as Adsorbent

On the basis of the above theory it is evident that the H or the OH ion concentration of a solution after adsorption may be far different from that of the solution before adsorption. A determination of the OH ion concentration of solutions of different salts with a common cation before and after adsorption should give an indication of the relative adsorption of the different anions, the adsorption being determined by the amount of OH ion set free. From Table XI page 25 it will be noted that the adsorbability of the several anions varied markedly.

On the whole it was found that negative radicals with hydrocarbon groups displaced OH^- more readily than did the inorganic radicals. All negative radicals were able to displace OH^- at least to some extent. Ions of metals less noble than H did not displace H^+ . Metals more noble than H did displace H^+ .

A salt in solution having a cation less noble than H when treated with carbon gave an alkaline reaction.

Adsorption of Acid Dyes by Carbon

Consider an acid dye such as sodium picrate to be of the general type $m\text{R}_a = m^+ + \text{R}_a^-$. The solution upon addition of carbon becomes alkaline. R_a^- displaces OH_s^- and is adsorbed, the solution becoming alkaline. With successive additions of dye solution the replacement of OH_s^- becomes less and less and throws successively less OH_s^- ion into solution.

Adsorption of Basic Dyes

As a general type take $\text{R}_c\text{A} = \text{R}_c^+ + \text{A}^-$ (*i. e.*, methylene blue). The reaction in this case progresses as follows: The cation readily displaces the

H_S^+ from carbon and the rate of reaction is rapid. The anion can displace OH_S^- from carbon but the reaction is less rapid and the displacing power is less than that of the cation R_C^+ with the result that with a small amount of dyestuff the acidity of the solution will decrease finally to neutral, but with higher concentration of dyestuff the adsorption of A^- will reach its maximum while R_C^+ continues to be adsorbed. This results in permanent acidity.

Adsorption *vs.* Chemical Constitution

According to the foregoing view it is seen that adsorption demands orientation of molecules at surfaces. Furthermore, in case the molecules are polar and contain COOH , CN , OH , Cl , or CONH_2 , etc., these groups would extend toward the water phase; in fact would probably exist in the outer double electrical layer. The addition of one or more of these groups to a molecule would tend to make it more polar, accordingly more soluble, with the result that the positive ion would tend to pass to the solution and less of it would be adsorbed for a given concentration. This we have seen to be the case. It has been found that benzoic acid is highly adsorbed. According to the above view we must consider the negative radical in contact with the carbon. The addition of an hydroxyl group to this compound decreased the amount adsorbed. The addition of the hydroxyl group to succinic acid likewise decreased the adsorption, while the addition of the second hydroxyl group decreased the adsorption still more. The introduction of the more polar amino group decreased the adsorption even more than the hydroxyl group. Similar results were obtained when the hydroxyl group was introduced into propionic acid. Introducing CH_2 groups into the anion increased its adsorption. The benzene ring structure likewise results in higher adsorption. We may consider then that an increase in hydrocarbon content results in a decreased solubility in water and at the same time it is probable that there results an increased affinity for the carbon. According to the above we can see that organic *i. e.*, carbon containing radicals are readily adsorbed. They may displace either H^+ or OH^- depending upon their charge.

Inorganic acids are but comparatively slightly adsorbed because the inorganic anion replaces more feebly the OH_S^- ion and inorganic bases are adsorbed scarcely at all, owing to the fact that cations of metals less noble than H do not displace H_S^+ from carbon. Thus we have no concentration of base at the interface.

IV. SUMMARY

1. Data have been presented in support of a theory of hydrolytic adsorption of electrolytes from solution by activated ash-free sugar charcoal.
2. Adsorption of methylene blue, a basic dye of the electrolyte type, by activated, ash-free sugar charcoal has been studied.

3. Evidence has been presented to show that this adsorption is partially, if not entirely, hydrolytic in nature.

4. It has been demonstrated that activated ash-free sugar charcoal will completely adsorb a certain maximum amount of methylene blue from solution and still leave the solution neutral. During this process of adsorption there is set free a considerable amount of hydrochloric acid which is readily and completely adsorbed. Adsorption of amounts of methylene blue greater than the above mentioned maximum results in the setting free of hydrochloric acid which is not subsequently removed from solution.

5. It has been demonstrated that the adsorption of acid dyes is accompanied by considerable hydrolysis and liberation of alkali which remains in solution.

6. The adsorption by this charcoal of a number of acids, bases, and salts has been investigated. It has been found that pure charcoal does not adsorb the strong inorganic bases. The adsorption of a salt of a strong base and a readily adsorbed acid results in the liberation of free base.

7. The effect on adsorption of the substitution of hydroxyl and amino groups in organic acids has been noted. The introduction of the hydroxyl group decreases the adsorption of the acid to a more or less marked extent, depending upon the nature of the acid into which it is introduced. The introduction of the amino group decreases the adsorption of the acid, the extent depending also upon the nature of the acid into which it is introduced. The effect of the amino group is considerably greater than that of the hydroxyl group.

8. A number of conflicting results of other investigators have been reproduced by means of neutral, activated, ash-free sugar charcoal and an explanation of their causes has been offered.

9. A theory of the mechanism of adsorption of electrolytes from solution by activated sugar charcoal has been presented.

